CONCENTRATION, MATRIX, AND WAVELENGTH DEPENDENCE IN THE PHOTOLYSIS EFFICIENCY OF MATRIX-ISOLATED BIACETYL

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The ultraviolet irradiation of matrix-isolated biacetyl ($C_4H_6O_2$) results in the formation of a complex of *trans*-methylhydroxycarbene (CH_3COH) and ketene (CH_2CO). Studies in this laboratory using pulsed sources have confirmed that these products arise from a two-photon process: the first photon ($\lambda < 450$ nm) places the molecule in the $\tilde{A}\ ^1A_u$ state, followed by relaxation to the long-lived $\tilde{a}\ ^3A_u$ state. Triplet-triplet excitation($\lambda < 550$ nm) from this state leads to the observed products.

The apparent quantum efficiency for the formation of these products was measured as a function of matrix (N_2, O_2, Ar, Kr, and Xe), dilution ratio for the parent compound, and wavelength of irradiation (using a continuous source). For all matrices, the apparent efficiency decreases with increasing $C_4H_6O_2$ dilution, indicating that the products may arise from a bimolecular process. No such effect was seen in $C_4D_6O_2$ experiments, which exhibit much lower levels of efficiency at all dilutions. The matrix has an effect on the high-dilution efficiency (N_2, $O_2 >$ Kr, Xe $>$ Ar), which suggests that the matrix participates in the H-transfer process.

Increasing the wavelength of irradiation from 436 to 450 nm results in an increase in the measured efficiency. At 436 nm, the reverse intersystem crossing ($\tilde{a}\ ^3A_u \rightarrow \tilde{A}\ ^1A_u$) channel is available to drain the triplet population. At 450 nm, this channel is no longer available, and the resulting increase in the steady-state triplet population leads to the observed enhancement.